

(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 2002335945 B2**

(54) Title
Method for coating a metal surface

(51) International Patent Classification(s)
C23C 22/48 (2006.01) **C23C 22/74** (2006.01)
C23C 2/04 (2006.01) **C23C 22/76** (2006.01)
C23C 2/06 (2006.01) **C23C 24/08** (2006.01)
C23C 2/26 (2006.01) **C23C 28/00** (2006.01)
C23C 22/73 (2006.01)

(21) Application No: **2002335945** (22) Date of Filing: **2002.10.25**

(87) WIPO No: **WO03/048403**

(30) Priority Data

(31) Number	(32) Date	(33) Country
2001/0787	2001.12.04	BE

(43) Publication Date: **2003.06.17**

(43) Publication Journal Date: **2003.08.21**

(44) Accepted Journal Date: **2008.04.03**

(71) Applicant(s)
Centre De Recherches Metallurgiques ASBL - Centrum Voor Research In De Metallurgie VZW

(72) Inventor(s)
Le Craz, Sebastien

(74) Agent / Attorney
Wray & Associates, Level 4, The Quadrant 1 William Street, Perth, WA, 6000

(56) Related Art
WO 2000/068460
US 5853850
JP 64-011983

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION
EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété
Intellectuelle
Bureau international



(43) Date de la publication internationale
12 juin 2003 (12.06.2003)

PCT

(10) Numéro de publication internationale
WO 03/048403 A1

(51) Classification internationale des brevets⁷ : C23C 2/26,
24/08, 2/04

(74) Mandataires : VAN MALDEREN, Michel etc.; Office
Van Malderen, Boulevard de la Sauvenière 85/043, B-4000
Liège (BE).

(21) Numéro de la demande internationale :
PCT/BE02/00162

(81) États désignés (*national*) : AE, AG, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ,
DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI,
SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC,
VN, YU, ZA, ZM, ZW.

(22) Date de dépôt international :
25 octobre 2002 (25.10.2002)

(25) Langue de dépôt : français

(26) Langue de publication : français

(30) Données relatives à la priorité :
2001/0787 4 décembre 2001 (04.12.2001) BE

(84) États désignés (*régional*) : brevet ARIPO (GH, GM, KE,
LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), brevet
eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet
européen (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), brevet
OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
MR, NE, SN, TD, TG).

Publiée :

— avec rapport de recherche internationale

En ce qui concerne les codes à deux lettres et autres abrévia-
tions, se référer aux "Notes explicatives relatives aux codes et
abréviations" figurant au début de chaque numéro ordinaire de
la Gazette du PCT.

(71) Déposant (*pour tous les États désignés sauf US*) : CEN-
TRE DE RECHERCHES METALLURGIQUES ASBL
- CENTRUM VOOR RESEARCH IN DE METAL-
LURGIE VZW [BE/BE]; Rue Montoyer 47, B-1000
Bruxelles (BE).

(72) Inventeur; et

(75) Inventeur/Déposant (*pour US seulement*) : LE CRAZ,
Sébastien [BE/BE]; Avenue Rogier 32/51, B-4000 Liège
(BE).

(54) Title: METHOD FOR COATING A METAL SURFACE

(54) Titre : PROCEDE DE REVETEMENT DE SURFACE METALLIQUE

(57) Abstract: The invention concerns a method for continuously coating a moving substrate, preferably a steel metal strip, said coating deposited on the substrate comprising an ultrafine thickness between 20 and 2000 nm, and preferably between 40 and 500 nm. The invention is characterized in that the deposition is based on an aqueous solution containing oxide nanoparticles, and carried out in controlled pH conditions at high substrate temperature, preferably higher than 200 °C, the duration of the deposition being less than 10 seconds, and preferably less than 2 seconds.

(57) Abrégé : La présente invention se rapporte à un procédé pour revêtir en continu un substrat en mouvement, de préférence une bande métallique en acier, ledit revêtement déposé sur le substrat comprenant une couche ultra-fine d'épaisseur comprise entre 20 et 2000nm, et de préférence entre 40 et 500nm, caractérisé en ce que le dépôt est réalisé: à partir d'une solution aqueuse contenant des nanoparticules d'oxydes; dans des conditions de pH contrôlé; à haute température de substrat, de préférence supérieure à 200 °C; la durée du dépôt étant inférieure à 10 secondes, et de préférence inférieure à 2 secondes.

WO 03/048403 A1

METHOD FOR COATING METAL SURFACES

Subject of the invention

- 5 [0001] The present invention relates to a method for continuously coating a substrate in motion, more particularly a metal sheet of coated or galvanised steel, by means of an ultra-thin protective layer of oxide nanoparticles, preferably silicon, titanium or zirconium.

10

Technological background

- [0002] The benefits of different materials such as zinc or aluminium are well known for the protection of steel sheets against corrosion. Numerous methods allow the
15 continuous deposition of a layer of zinc or of aluminium onto a sheet passing through a bath containing one or the other of these metals or one of their alloys in a molten state. These deposits obtained by immersion generally have a thickness of 5 to 25 microns.

- 20 [0003] Thinner deposits, at the most of a few microns, can be achieved by electro-deposition or sometimes from the vapour phase of the protective metal.

First approach: coating without chromate

- 25 [0004] After the provision of anticorrosion protection by the layer of zinc or another expendable metal described above, it is necessary to achieve a further layer which at the same time facilitates the attachment of a possible subsequent coating and in addition protects the
30 surface of the coated metal against changes of aspect in the course of storage. Several types of coating are known, among which phosphate treatments with zinc, alkaline treatment, silanation, treatment with chromate, etc. The

choice of a specific treatment depends on the type of use for which the product is intended.

[0005] At the present time, the best resistance against corrosion is obtained with methods including at least one chromic rinse. Unfortunately, the hexavalent chrome that is used in these treatments is a very toxic substance whose use is increasingly subjected to regulation. In view of this situation, a growing demand for steels coated without hexavalent chrome is observed.

10

Second approach: coil-coating at the end of the galvanisation line

[0006] One of the techniques allowing to apply undercoat and paint in a particularly effective manner is the "coil-coating" technique, that is to say the continuous deposition of an organic coating on a sheet in motion which is re-coiled at the end of the line. However, these days, the painting operation is most often dissociated from the galvanisation operation. This situation is explained by the great difficulty of applying paint on lines as fast as galvanisation lines. Thus, the deposition of paint is performed either by the buyer of the metal plates or on lines exclusively dedicated to pre-treatment and painting.

[0007] Enormous joint efforts of metallurgists and paint manufacturers aim to simplify the methods for depositing paints so as to make them practical at high speed. The aim is to be able to apply a metal coating, such as zinc or another metal, and paint on the same line. The benefits of such a combination are multiple. Firstly, the use of oil for anticorrosion protection of the sheet during storage or transport is eliminated. In addition, the number of installations and in particular the major investment and maintenance costs associated with uncoiling and re-coiling are reduced.

Promising solutions: oxide of silicon, titanium, zirconium, aluminium, cerium or antimony

[0008] If the methods for producing the protective
5 layer of metal surfaces, whether coated or not, are
examined, oxides of silicon, titanium, zirconium,
aluminium, cerium or antimony are very promising compounds.
They are first of all resistant to oxidants. They are also
electrical insulators and moreover, they are relatively
10 inert from a chemical point of view. Thus, an ultra-thin,
dense layer of this type of oxides could suffice to ensure
good protection against corrosion.

[0009] Paradoxically, it is known that metal
surfaces always bear an oxide film but that, in its natural
15 form, it cannot really be used to fulfil the functions of
protection and attachment. Indeed, procedures such as hot
galvanisation or thermal oxidation lead to the formation of
oxides, for instance of zinc or of aluminium, on the
surface of steel sheets. However, this protection is weak
20 and these oxides are moreover inert and do not allow, or do
not allow so well, the subsequent attachment of an organic
coating such as paint (see for example "Le livre de
l'acier" (The book of steel), G. BERANGER et al., Ed.
Lavoisier Tec & Doc (1996) pp. 700-701). In order to
25 overcome this difficulty, one may take the trouble to
chemically transform the galvanised surface, achieved by
the dissolution and/or removal of these inert oxides, into
a reactive surface available for subsequent coating.

[0010] The above-mentioned beneficial oxides (of
30 silicon, etc.) have the advantage of being both compatible
with metals and with the organic materials used in the
composition of paints. Indeed, the Applicant noted that
these oxides and the metal surfaces to be protected may, in
certain conditions, chemically bond via an oxygen bridge.

Likewise, with the formation of organic silanes, it is possible to obtain covalent bonds of great energy between organic molecules and oxides of this type. The latter therefore make ideal candidates for allowing an excellent
5 bond between the substrate and paint.

[0011] Moreover, the need to find new methods for coating galvanised steels has increased the importance of the chemical compounds that had been neglected up to now.

[0012] Thus, nanoparticles which have however been
10 commercially available for over 60 years have only been actually incorporated as a principal component of a treatment layer before paint for a dozen years or so.

[0013] The advantages of the use of nanoparticles are multiple. First of all, they are less reactive than
15 molecular precursors such as silanols, mineral salts or the organometallic precursors and therefore allow to achieve far more stable solutions. Furthermore, they are sufficiently small to allow the creation of ultra-thin coatings (a few hundred nanometres). In addition, their use
20 allows the production of more malleable coatings than dense coatings (for instance in molten glass). Lastly, although solutions of these nanoparticles are classified as corrosive or harmful, they are neither toxic nor dangerous to the environment as solutions based on hexavalent chrome
25 can be.

State of the art

[0014] Attempts at wet deposition of ultra-thin coatings of, amongst other things, silica nanoparticles,
30 have been carried out but these tests have proved to be unsatisfactory in terms of reaction speed. The deposition speed must in fact be very rapid because the coating must be achieved on the galvanising lines themselves, the speed of which is typically 2 or 3 metres a second.

[0015] Amongst other attempts, one may cite:

- the deposition of a ethysilicate/silica mixture (sol-gel technology) on aluminium; this method requires slow drying, hence takes a long time, in order to limit the formation of cracks when the solvent evaporates (American patents US-A-5 514 211 and US-A-5 879 437 in the name of Alcan Inc.);
- the rinse, which also takes a long time, in a solution of silicate/metallic salt followed by a treatment based on silane, which is necessary given the lack of energy supplied to the system. This method has been developed by Armco Steel and is the subject of European application EP-0 492 306-A2;
- the immersion of coated parts in a mixture based on a mineral or organic silicate, generally of potassium silicate. This operation is carried out at a slightly higher temperature (125°C). Good properties of resistance against corrosion are claimed but the attachment of subsequent coatings is not taken into account and the treatment times are still long since times of up to 60 seconds are reported. This method was patented by Zaclon Corporation (US-A-5 068 134);
- the treatment of galvanised steel in a solution mainly containing nanometric silica, followed by a drying operation. Patent applications were filed by NKK Corp. (JP-A-92 96276 or JP-A-92 96277); here again the drying time is prohibitive;
- the treatment of galvanised steel by a solution of oxide particles or a mixture of oxide (SiO_2 , Sb_2O_3 , Al_2O_3 , ZrO_2 or TiO_2) the surface of which adsorbs Ni or Co ions. A drying operation is also required here (patent application JP-A-21 04675 filed by Sumitomo Metal Ind. Ltd.)

[0016] In each of the solutions proposed above, the fact of working at low temperatures implies a low speed of conglomeration of the nanoparticles. The lack of energy does not favour good bonding of the particles to each other either. This will eventually have consequences on the cohesion of the layer which will have a tendency to turn out brittle.

[0017] Other solutions have been proposed, in particular electrolysis treatments. This type of method is effective since thermal energy is replaced by electricity:

- the deposition of a zinc-silica compound on a steel plate by electrolysis by means of a solution containing colloidal silica, surfactants and zinc salts. The morphology of the coating is not the same as that of a coating of pure silica. There are in particular far less attachment points for an organic coating layer such as paint (American patent US-A-4 655 882 by Okayama – Ken);
- the production of a layer of Cr oxide/nanoparticles of silica on a galvanised plate by cathode electrolysis. Here, the silica plays the part of a matrix for the coating. Unfortunately, this method requires the use of Cr (VI) (European patent application EP-0 247 290 by Kawasaki Steel).

The discussion of the background art is included exclusively for the purpose of providing a context for the present invention. It should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was common general knowledge in the field relevant to the present invention in Australia or elsewhere before the priority date.

Throughout the specification and claims, unless the context requires otherwise, the word “comprise” or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Aims of the Invention

[0018] The present invention aims to provide a method for coating a metal with an ultra-thin protective oxide deposit, preferably of silicon, titanium, zirconium, cerium, yttrium or antimony.

- 5 [0019] A complementary aim of the invention is to provide an alternative method to the current procedures relying on the use of materials listed as toxic, in particular a method which does not use chrome(VI).

[0020] Another aim of the invention is to provide a method which is very quick and easy to implement, in particular capable of being implemented in the context of the "coil coating" technique.

Main characteristics of the invention

5 [0021] A first aim of the present invention relates to a method for continuously coating a substrate in motion, such as for instance a metal sheet of coated steel, said coating being deposited on the substrate comprising a layer of ultra-thin thickness between 20 and 2000nm, and preferably between 40 and 500nm, characterised in that the deposition is achieved:

- 10
- from an aqueous solution containing oxide nanoparticles,
 - in conditions of controlled pH,
 - at high temperature, preferably higher than 200°C,
 - the deposition time being less than 10 seconds, and preferably less than 2 seconds.

15 In one aspect of the invention, there is provided a method for the continuous coating of a substrate in motion, preferably a steel sheet, said coating deposited on the substrate comprising an ultra-thin layer of a thickness between 20 and 2000nm, and preferably between 40 and 55nm, the deposition being achieved without chromate:

- 20
- from an aqueous solution on one or several types of oxide nanoparticles selected from the group comprising SiO₂, TiO₂, ZrO₂, Al₂O₃, CeO₂, Sb₂O₅, Y₂O₃, ZnO and SnO₂ and having a size between 1 and 100 nm,
 - at a substrate temperature higher than 200°C,
 - the deposition time being less than 10 seconds, and preferably less than 2 seconds,

characterised in that the pH of the aqueous solution is controlled and maintained between 9 and 13.

[0022] According to the invention, the deposition is achieved on a substrate of bare metal, preferably steel, aluminium, zinc or copper, or of a first metal coated by a
5 second metal, preferably a steel sheet covered with a layer of zinc, aluminium, tin or an alloy of at least two of these metals.

[0023] As an advantage, the nanoparticles comprise oxides, preferably SiO_2 , TiO_2 , ZrO_2 , Al_2O_3 , CeO_2 , Sb_2O_5 , Y_2O_3 , ZnO , SnO_2 or mixtures of these oxides, are hydrophilic and/or hydrophobic, have a size between 1 and 100nm and are included in the solution at a
10 density between 0.1 and 10%, and preferably between 0.1 and 1%.

[0024] According to an important characteristic of the invention, the pH of the solution is adjusted so as to allow the dissolution and/or removal of surface oxides on the metallic substrate during its contact with the solution

and to give the particles present in the solution a sufficient electrical charge. Thus, any conglomeration in the solution is hopefully avoided and the particles are made as reactive as possible without destabilising the solution.

[0025] In addition, the pH of the solutions based on nanoparticles of SiO_2 , SnO_2 , TiO_2 , ZnO , Sb_2O_5 or of mixtures thereof is basic, and preferably between 9 and 13, whereas the pH of solutions based on nanoparticles of ZrO_2 , CeO_2 , SiO_2 , Sb_2O_5 or mixtures thereof is acid, and preferably between 1 and 5.

[0026] Preferably, the pH of solutions based on a mixture of nanoparticles is adjusted so that the solution is stable during its period of use.

[0027] Still more preferably, in cases where the substrate has a surface layer comprising a compound of zinc, aluminium, iron, tin, chrome, nickel or copper, the pH of the solution may be basic. Similarly, in cases where the substrate has a surface layer comprising a compound of zinc, aluminium, iron, tin, chrome, nickel or copper, the pH of the solution may be acid.

[0028] According to a first preferred embodiment of the invention, the deposition is achieved by immersion of the substrate for a controlled period in an immersion tank containing the solution.

[0029] According to a second preferred embodiment of the invention, the deposition is achieved by spraying the solution over the substrate by means of one or more jets. By jet(s) is meant any system, assisted by compressed gas or not, which sprays droplets of the solution.

[0030] According to a third preferred embodiment of the invention, the deposition is achieved by depositing the solution on the substrate by means of a roller.

[0031] Preferably, the solution which comes into contact with the sheet is maintained at a temperature below 50°C, and preferably below 35°C and the temperature of the substrate at the start of the deposition is higher than
5 200°C.

[0032] Still preferably, when the substrate already has a metallic coating before treatment, the temperature of the substrate at the start of the deposition is higher than 200°C and lower by 30 to 100°C than the melting point of
10 said coating metal.

[0033] According to a particular characteristic of the invention, when the substrate has a metallic coating obtained by immersion, preferably by galvanised hot dipping, the deposition is achieved just after the metal
15 deposition.

[0034] According to another characteristic of the invention, in cases where substrates already have a metal coating produced by immersion, said substrate is protected from significant contact with the air.

20 [0035] As an advantage, the deposition is limited in time by varying the depth of immersion in the case of a deposition in a solution or the length sprayed in the direction of the flow in the case of spraying the solution with (a) jet(s).

25 [0036] According to a general aspect of the invention, the solvent used comprises water with possibly a co-solvent capable of dispersing the nanoparticles in an effective manner.

[0037] As an advantage, agents are added to the
30 solution of nanoparticles in order to improve the resistance against corrosion and/or the adhesion to the substrate or paint and/or to improve the flow during formation.

[0038] After further investigation, the inventors noted that the coated substrate may be rinsed after coating with water or with a solution based on organic silanes or carboxylic acid containing an function capable of subsequently forming a strong organic bond.

[0039] It is moreover advantageous for the method of the invention to comprise means for:

- measuring and controlling the pH continuously,
- ensuring that the solution is renewed and that excess products of the reaction are eliminated,
- ensuring the homogeneous mixture of the bath so as to avoid turbulence at its surface.

[0040] More specifically, as in the first preferred embodiment, the temperature of the sheet and of the bath is controlled, as are the time that the sheet stays in the bath, the concentration of nanoparticles in the bath and the pH of the bath.

[0041] More specifically, according to the second preferred embodiment, the temperature of the sheet, the spraying time, the concentration of the nanoparticles in the sprayed solution, the flow rate of the spray and the pH are controlled.

[0042] Another significant advantage of the coating method of the present invention is that it does not require any additional drying operation after the production of the coating per se.

[0043] A second aim of the present invention relates to an installation for the coating of a steel sheet by hot dipping, comprising a device for producing a second coating layer by the implementation of the method in the invention, characterised in that said device is located after the units ensuring the spinning and solidification operations of the first coating layer, said method being carried out in this device at a temperature about 100°C

below the solidification temperature, preferably between 200 and 350°C.

[0044] Finally, a third aim of the present invention relates to a flat or long metal product, preferably a sheet, thread, panel or tube, coated with an ultra-thin protective deposit by means of the method in the invention, characterised in that said protective deposit comprises nanoparticles of oxides or a mixture of these oxides, preferably SiO_2 , TiO_2 , ZrO_2 , Al_2O_3 , CeO_2 , Sb_2O_5 , Y_2O_3 , ZnO or SnO_2 , without hexavalent chrome and has a thickness between 20 and 2000nm, preferably between 40 and 500nm.

Detailed description of the invention

[0045] The present invention aims to provide a method for coating metal surfaces so as to create a surface layer which ensures the protection and at the same time the ability to attach a subsequent layer. The substrate to be coated by an ultra-thin protective layer is either a bare metal such as steel, aluminium, zinc, copper, etc. or a metal coated with a layer of another metal, such as a layer of zinc, aluminium, tin or an alloy of these metals.

[0046] According to the invention, this treatment is characterised by the use of oxide nanoparticles.

[0047] The particles used are preferably the following oxides: SiO_2 , TiO_2 , ZrO_2 , Al_2O_3 , CeO_2 , Sb_2O_5 , Y_2O_3 , ZnO , SnO_2 . They are either pure or in the form of a hydrophilic and/or hydrophobic mixture. The size of the particles is between 1 and 100nm. The solvent used is either water or alcohol, or even a mixture of water and alcohol. Another solvent which can disperse the nanoparticles in an effective manner may also be used.

[0048] Various deposition techniques may be used:

- immersion for a controlled period in an immersion tank;

- spraying a solution (vaporiser, jets), that is to say propulsion under the effect of the pressure of the solution or by a carrier gas under pressure;
- deposition with a roller ("roll coater")

5 [0049] The production of an ultra-thin layer is associated with deposition times of less than 5-10 seconds, and preferably 2 seconds. In addition, a short time is required since the temperature of the substrate falls during the deposition; it is vital to use a short time
10 period in order to dry the sheet by the heat present there because of its own temperature at the end of the treatment. This type of "natural" drying in fact avoids the risk of damaging the coating by forced external drying.

[0050] The temperature of the substrate plays an
15 important role in the method in the invention. Preferably, if the temperature is higher than 200°C, one may benefit from the temperature of the sheet in the case of coating by immersion. In this case, indeed, the sheet is continuously tempered in an oven, immersed in the bath of liquid metal,
20 then, after the spinning and solidification of the coating, it is still at a high temperature. However, it still cannot be cooled too quickly because that would affect its evenness. According to an important characteristic of the invention, the deposition will be achieved with a substrate
25 temperature of the order of the temperature at which the coating metal solidifies less about 30 to 100°C.

[0051] According to the present invention, the
conglomeration of particles on the metal sheet is mainly achieved in the first second of contact between the above-
30 mentioned solution and the hot sheet, for example in an immersion bath. With the time in the bath preferably less than 2 seconds, the residual heat of the plate at its exit from the tank allows rapid "self-drying" of the coating layer formed.

[0052] In the case of an uncoated metal, one may in certain cases benefit from the stored heat of the metal, for instance, in continuous tempering of the steel sheets, high temperature cleaning, etc. The metal to be treated can
5 also be heated with a flame, by induction, etc.

[0053] As for the temperature of the solution, it will affect its reactivity and stability, as well as the cooling speed. It will be maintained before the deposition at a temperature below 50°C, and preferably below 35°C.

10 [0054] The pH of the solution at the moment of the deposition represents a crucial aspect since it affects the attachment of the present treatment to the metal surface, whether coated or not. The presence of a non-protective oxide such as Al_2O_3 or ZnO on the surface of zinc is,
15 according to the Applicant, not a good thing. Therefore, its removal is a priority. To this end, the colloidal solution of nanoparticles is modified by the addition of a basic compound such as soda, potassium hydroxide or ammonium carbonate. The resulting increase in pH is
20 intended to make the surface oxide present soluble by forming a hydroxide. The boiling of water at the surface of the zinc then easily wipes away this compound and cleans the surface of all pre-existing or unwanted oxides. It is intended to electrically charge to the maximum the
25 nanoparticles of the surface to be coated in order to avoid any conglomeration in the colloidal solution and to make the particles as reactive as possible without destabilising the solution. To this end, it is recommended that the pH of the solutions used is adjusted.

30 [0055] In the case of substrates already having a metal coating produced by immersion, the substrate is protected from significant contact with the air so as to prevent the formation of a too thick layer of inert oxides.

This could not in fact be removed within acceptable treatment times on line.

[0056] This increase in pH also has other advantages. It makes the silica more reactive thanks to a
5 thicker surface concentration of silanolate. Moreover, according to certain sources, this would allow the production of dense coatings. The best results in terms of the coating adhesion and powdering are obtained with pH's between 9 and 13. With pH's of less than 9, the silica is
10 powdery and adheres poorly. With a pH higher than 13, the colloidal solution becomes unstable: the silica polymerises and falls off by itself.

[0057] The use of alkaline baths is recommended with solutions of nanoparticles of oxides such as SiO_2 ,
15 SnO_2 , TiO_2 , ZnO or Sb_2O_5 . On the contrary, with solutions based on nanoparticles of oxides such as ZrO_2 , CeO_2 or again SiO_2 and Sb_2O_5 , their use is recommended with an acid pH, and preferably between 1 and 5.

[0058] However, solutions of either basic or acid
20 pH may be used if the substrate comprises a compound of zinc, aluminium, iron, tin, chrome, nickel or copper.

[0059] Table 1 shows the influence of the pH of a colloidal solution of silica nanoparticles on the subsequent adhesion of paint, in the case of galvanised
25 plates pre-treated from said colloidal solution with different values of pH.

Table I

Adhesion	pH 7	pH 9	pH 11	pH 12
Grid pattern + tape (*)	-	-	0	+
Bending OT + tape (**)	-	0	0	+

Key: - large visible surface of bare metal

0 small visible surface of bare metal

+ no surface of bare metal exposed, no trace of paint
on the tape

5

(*) scratch test with a comb so as to make a grid pattern on the paint followed by an adhesion test with scotch tape;

(**) test: bending of the plate by 180°, the radius of the curve of the bend not allowing the insertion of a same plate into the bend. Followed by an adhesion test with scotch tape.

10

[0060] With regard to the chemistry of the deposition bath, on the one hand the concentration on particles in the bath is between 0.1 and 10%, and preferably between 0.1 and 1%. On the other hand, from the point of view of the chemical management of the treatment bath, means are provided for the continuous measurement and control of the pH, renewal of the solution, removal of the reaction products and an adjusted mixing system in order to prevent turbulence at the surface of the bath, it being understood that the surface of the bath must be as even as possible.

15

20

[0061] The thickness of the deposit is typically 20 to 5000nm, preferably between 50 and 1000nm. The thickness is for instance controlled by ellipsometric measurements in line or by nuclear measurements. In the case of immersion in a bath, the control parameters are specifically the temperature of the sheet and of the bath, the time that the sheet stays in the bath, the concentration of nanoparticles and the pH of the bath. In the case of spraying with jets, the control parameters are specifically the temperature of

25

30

the sheet, the spraying period, the concentration of the nanoparticles in the vaporised solution, the flow rate of the sprays and the pH.

[0062] Additives may be added to the basic
5 particles:

- either to improve the resistance against corrosion (based on organic or mineral compounds such as CrX, MoX, etc.)
- or to improve flow during formation (MoS₂, PTFE, etc).

[0063] After deposition, it may be worth rinsing
10 with an aqueous solution at a few parts per thousand of organic silane. There are two reasons for doing this: firstly, to obtain a good rinse of the excess silica and then to benefit from the opportunity to give certain functions of organic substances of the type amine, alcohol,
15 epoxy or even double carbon-carbon bond (for example acrylate) to the surface of the oxide layer. This allows the subsequent strengthening of the silica/organic substance bond.

20 Description of a preferred embodiment of the invention

[0064] By way of an application example of the invention, a continuous coating line for a steel sheet will be described below.

[0065] A continuous line for coating by immersion
25 generally comprises the following successive steps:

- the sheet continuously passes through a tempering oven;
- it is then plunged into a bath of liquid metal which is intended to coat it;
- upon its exit from the bath, the sheet follows a vertical
30 route: first, the excess coating metal is removed from it by gas spinners and then this coating solidifies while the sheet moves up to the upper roller;
- lastly, the sheet passes through a section where the following operations are performed: cooling by air, mist

and/or immersion in water, cold-rolling, conversion of the surface (chroming).

[0066] The speed of the line is typically of the order of 120 m/min (i.e. 2 m/sec). The sheet temperature is
 5 of the order of 460°C in the bath. In the case of galvanised coating, the temperature gradually falls so as to reach 340-390°C at the upper roller; it then falls progressively. In the case of "galvanneal" coating (ZnFe alloy), the sheet is immediately reheated after spinning to
 10 490-560°C, then it is cooled again before it reaches the upper roller.

[0067] In such a line, the coating may be applied for example:

- by spraying during the vertical movement of the sheet
 15 towards the upper roller or just after this roller, the temperature of the sheet at this point being typically between 200 and 350°C;
- by immersion in a bath of solution during a descending vertical movement.

20 [0068] The treated surfaces are metals or alloys which may be made of iron (steels), aluminium, zinc or copper as well as stainless steels. It is also very interesting to use this coating method to protect coated surfaces such as galvanised steels (that is to say steels
 25 coated with an alloy based on zinc or aluminium).

[0069] The method of the invention can be applied to any metal piece of a particular shape (for example tubes, panels, threads, etc.) but also to metal sheets which will be cut into plates.

30 [0070] The production of this layer gives the advantage of protecting the substrate against premature deterioration caused by aggressive external agents (chemical, thermal, mechanical, etc.). This coating also has the advantages of:

- limiting the formation of corrosion;
- creating an electrically insulating layer, especially intended for application to plates used in electrical and electronic construction;
- 5 - ensuring protection against fingerprints during production or service;
- improving the resistance of the product against scratches and abrasion.

[0071] The coating in the invention also has the
10 advantage of helping the metal to withstand the various treatments which it will subsequently undergo, and in particular:

- of improving the adhesion of organic coatings subsequently added in order to protect or give a
15 different aspect (colour, shine, etc.);
- of improving the strength of glued assemblies;
- of improving suitability for shaping.

[0072] The method of the invention also has the advantage that it can be used in a very short time
20 interval. This short time is required on the one hand because of the rapid processing on the line (and thus with a limit to the length of the bath or the spraying) and on the other hand because of the product itself, which requires that the reaction of the coating formation is
25 rapid. This choice made by the Applicant is deliberate and linked to the constitution and structure of the layer formed.

[0073] According to the invention, the drying after coating being very rapid, it turns out that the sheet can
30 be directly sent onto a "skinpass" line (a series of damp rollers) intended to modify the mechanical properties of the sheet without any additional drying operation. In this respect, the invention has the advantage over the present state of the art that, in the case of a long time in the

bath, the plate loses its heat in the bath and an additional drying unit must be provided (see for example JP-A-92 96275).

[0074] Apart from these requirements, the method of
5 the invention allows to meet the current requirements in
terms of environmental protection ("chrome-free" methods)
and simplification of processes.

CLAIMS

1. Method for the continuous coating of a substrate in motion, preferably a steel sheet, said coating deposited on the substrate comprising an ultra-thin layer of a thickness between 20 and 2000nm, and preferably between 40 and 55nm, the deposition being
5 achieved without chromate:
- from an aqueous solution on one or several types of oxide nanoparticles selected from the group comprising SiO₂, TiO₂, ZrO₂, Al₂O₃, CeO₂, Sb₂O₅, Y₂O₃, ZnO and SnO₂ and having a size between 1 and 100 nm,
- at a substrate temperature higher than 200°C,
- 10 the deposition time being less than 10 seconds, and preferably less than 2 seconds.
- characterised in that the pH of the aqueous solution is controlled and maintained between 9 and 13.
2. Method as in Claim 1, characterised in that the deposition is achieved on a substrate of a bare metal, preferably steel, aluminium, zinc or copper, or of a first metal
15 coated with a second metal, preferably a steel sheet covered with a layer of zinc, aluminium, tin or an alloy of at least two of these metals.
3. Method as Claim 1 or 2, characterised in that the pH of said solution is adjusted so as to allow the surface oxides on the metal substrate to be dissolved and/or removed during its contact with the solution and to give the particles present in the solution an
20 electrical charge sufficient to prevent conglomeration.
4. Method as in Claim 1, 2 or 3, characterised in that the pH of the solutions based on a mixture of nanoparticles is adjusted so that the solution is stable during its period of use.

5. Method as in any one of Claims 1 to4, characterised in that the deposition is achieved by immersion of the substrate for a controlled period of time in an immersion tank containing the solution.
- 5 6. Method as in any one of Claims 1 to4, characterised in that the deposition is achieved by spraying the solution onto the substrate by means of one or several jets.
7. Method as in any one of Claims 1 to4, characterised in that the deposition is achieved by deposition of the solution onto the substrate by means of a roller.
8. Method as in any one of Claims 5 to7, characterised in that the solution that comes into contact with the sheet is maintained at a temperature lower than 50°C and preferably
10 lower than 35°C.
9. Method as in any one of the preceding claims, characterised in that, when the substrate already has a metal coating before treatment, the temperature of the substrate at the start of deposition is higher than 200°C and lower by 30 to 100°C than melting temperature of said coating metal.
- 15 10. Method as in Claim9, characterised in that, when the substrate already has a metal coating obtained by immersion, preferably by galvanised hot dipping, said deposition is achieved just after the deposition of the metal coating.
11. Method as in Claim10, characterised in that, in the case of substrates already having a metal coating obtained by immersion, said substrate is protected from significant
20 contact with the air.
12. Method as in any one of the preceding claims, characterised in that the deposition is limited in time by varying the depth of immersion in the case of a deposition in a solution or the length sprayed in the direction of the flow in the case of spraying the solution with jet(s).

13. Method as in any one of the preceding claims, characterised in that the solvent used comprises water with possibly at least one co-solvent which can disperse the nanoparticles in an efficient manner.

5 14. Method as in any one of the preceding claims, characterised in that agents are added to the solution of nanoparticles in order to improve the resistance against corrosion and/or the adhesion with the substrate or paint and/or to improve the flow during formation.

10 15. Method as in any one of the preceding claims, characterised in that the coated substrate may be rinsed after coating by means of water or of a solution based on organic silanes or carboxylic acid with a function that can subsequently form a strong organic bond.

16. Method as in Claim5, characterised in that it comprises means for:

- continuously measuring and controlling the pH,
- 15 - ensuring that the solution is renewed and that excess products of the reaction are removed,
- ensuring the homogenous mixture of the bath so as to prevent turbulence on its surface.

20 17. Method as in Claim16, characterised in that the temperature of the sheet and of the bath is controlled, as are the time the sheet stays in the bath, the concentration of nanoparticles in the bath and the pH of the bath.

18. Method as in Claim6, characterised in that the temperature of the sheet is controlled, as are the spraying time, the concentration of nanoparticles in the solution sprayed, the flow rate of the spray and the pH.

19. Method as in any one of the preceding claims, characterised in that it does not require any additional drying operation after the production of the coating per se.